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Effect of organic impurities on the nucleation parameters of KDP single crystals

C levan

Physics Research Centre, S T Hindu College,
Nagercoil-629 002, Tamilnadu, India

E-mail : maha@sancharnet in

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Abstract : Induction periods have been measured for various supersaturated aqueous solutions of potassium dihydrogen orthophosphate (KDP) added separately with glycine and thiourea by the direct vision method Various critical nucleation parameters have been calculated based on the classical theory for homogeneous crystal nucleation. The critical nucleation parameters increase with the increase in concentration of impurity in the KDP solutions.

Keywords : Nucleation parameters, impurity added KDP crystals, induction periods

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Potassium dihydrogen orthophosphate (abbreviated as KDP), KH_2PO_4, belongs to the scalenohedral (twelve - sided polyhedron) class of tetragonal crystal system and has created considerable interest among several research workers. It has the tetramolecular unit cell having the dimensions [1] given as $a = b = 7.448$ Å and $c = 6.977$ Å.

The induction period (τ) can be measured and used [2, 3] to calculate certain critical nucleation parameters like interfacial tension of the solid relative to its solution, energy of formation of a critical nucleus, and size of the nucleus in equilibrium with its solution, based on the classical theory for homogeneous crystal nucleation. Nucleation process is the initial and important phenomenon in liquid – solid phase transition.

In a previous study, we [3] have shown that we cannot restrict the shape of the critical nucleus to a sphere. Our studies on ammonium dihydrogen orthophosphate (ADP) and urea nitrate crystals show that it would be better to consider the shape of the critical nucleus as cylindrical than cubic and spherical. Recently, Freeda and Mahadevan [4] also found that the cylindrical shape is better to be considered.

Joshi and Antony [5] have studied the nucleation kinetics of pure KDP crystals in aqueous solutions. Effect of various types of inorganic impurities (having and not having any common ion with KDP) on the nucleation parameters of KDP, has been studied by several workers [4, 6 - 10]. However, no attempt has been made so far to study the effect of organic impurities.

We have attempted in the present work, to study the effect of two simple organic compounds, *viz.* thiourea (CH_4N_2S) and glycine ($C_2H_5NO_2$) as impurities (added in the solution with impurity concentration in the range of 2000 to 10000 ppm *i.e.* 0.2 to 1.0 mole %) on the nucleation parameters of KDP. Induction periods were measured for various supersaturated aqueous solutions by the direct vision method. Various critical nucleation parameters were calculated based on the classical theory for homogeneous crystal nucleation assuming the shape of the critical nucleus as cylindrical. ΔG is the energy of formation of the nucleus. r and h are respectively, the radius and height of the nucleus: σ and σ_0 are the interfacial tensions, respectively for curved and flat surfaces of the nucleus. We report and discuss here results of the present study.

Analytical reagent grade (AR) samples of KDP, thiourea and glycine along with double - distilled water were used in the present study. Aqueous solutions of various supersaturated concentrations (x) (2.0, 2.1, 2.2 and 2.3 M) were prepared by dissolving the required amount of KDP and the impurity at a temperature slightly higher than the saturation temperature (33°C). Supersaturation was obtained by natural cooling.

Induction periods were measured and critical nucleation parameters were calculated following the procedures reported earlier [3]. Experiments were performed with six different KDP : impurity molecular ratios, *viz.* 1 : 0.0 (pure KDP), 1 : 0.002, 1 : 0.004, 1 : 0.006, 1 : 0.008 and 1 : 0.010 (*i.e.* impurity concentrations are respectively 0, 2000, 4000, 6000, 8000 and 10000 ppm). Volume of the solutions taken in the nucleation cell was maintained at 20 ml in all the experiments in the present work. Several nucleation runs were carried out under controlled and unstirred conditions. Reproducible results within an accuracy of ± 2.5 % were obtained. The supersaturated concentration was so considered for providing an induction period of at least 50 s.

The results obtained in the present study are provided in Table 1. τ, ΔG, r and h values are given only for the maximum supersaturated concentration (2.3 M).

For both the impurities considered in the present study, the values of τ decreased and hence, the nucleation rate increased as the supersaturated concentration of the aqueous solution increased. It was also observed that the values of ΔG, r and h decreased when the supersaturation increased. This is similar to that observed by previous authors for their systems.

Plots of $\ln \tau$ *versus* $1 / \ln^2 (x / x_0)$ (not shown here) are nearly linear for pure and glycine added systems. This is similar to that observed for pure KDP by Joshi and Antony [5] and $(NH_4)_2SO_4$ and NH_4Cl added KDP by Freeda and Mahadevan [4]. However, significant deviations from linearity are observed at lower supersaturation levels for thiourea added KDP. Similar non-linearity has also been observed for KDP added with $KClO_4$, K_2CrO_4, KBr, $K_2Cr_2O_7$, KNO_3, KCl, ADP and NH_4NO_3 [4, 7 - 10]. It has been shown [4] that this deviation is caused by the heterogeneous nucleation due to impurities. As done by the earlier workers, in order to reduce the effect of heterogeneous nucleation on the nucleation parameters, the results were obtained using the slope determined in the linear region of the plots.

In both the impurity added systems considered in the present study, it can be noticed (see Table 1) that the induction period decreased with the increase in impurity concentration. For all the impurities studied so far, it was found that the presence of impurity in the KDP solution decreased the induction period. The increase in the concentration of impurity further decreased the induction time. The effects of soluble impurities may be caused by changing the equilibrium solubility or the solution structure, by adsorption or chemisorption on nuclei or heteronuclei by chemical reaction or complex formation in the solution and so on. The effects of insoluble impurities are unpredictable [2].

It can be seen from Table 1 that the nucleation parameters increase with increase in impurity concentration. This is similar to that observed [4, 7 - 10] for KDP added with $KClO_4$, KBr, K_2CrO_4, $K_2Cr_2O_7$, NH_4Cl, NH_4NO_3, ADP and $(NH_4)_2SO_4$. Freeda and Mahadevan [4] have analysed the effect of inorganic impurities on the nucleation parameters of KDP and made three statements related to the variation of nucleation parameters with the concentration of impurities in the solution. It can be stated that in the case of KDP added with thiourea and glycine (organic impurities having no common ion with KDP), the nucleation parameters increase with the impurity concentration regardless of density or lattice size of the impurity.

Hence, with the available data on inorganic and organic impurities, we update the statements of Freeda and Mahadevan [4] as

(i) For KDP added with impurities having common cation (K^+), the nucleation parameters increase with impurity concentration for the denser impurities and decrease with the impurity concentration for the rarer impurities;

Table 1. Results obtained in the present study *

Impurity concentration (mole %)	τ (s)	ΔG (kJmole-1)	r (nm)	h (nm)	σ_0 (mJm^{-1})	σ (mJm^{-1})
a) For pure KDP	774	9.654	0.618	0.906	5.530	7.550
b) For thiourea added KDP						
0.2	200	11.657	0.657	1.315	5.899	8.048
0.4	170	11.737	0.658	1.318	5.912	8.066
0.6	115	12.557	0.674	1.348	6.047	8.250
0.8	75	14.177	0.702	1.404	6.297	8.591
1.0	55	15.080	0.716	1.433	6.427	8.768
c) For glycine added KDP						
0.2	712	10.136	0.628	0.920	5.620	7.670
0.4	602	10.215	0.629	0.923	5.640	7.690
0.6	532	10.588	0.637	0.934	5.700	7.780
0.8	434	10.757	0.640	0.939	5.730	7.820
1.0	319	11.251	0.650	0.953	5.820	7.940

* τ, ΔG, r and h values are given only for the maximum supersaturated concentration (2.3 M)

(ii) For KDP added with isomorphous impurities, the nucleation parameters increase with the impurity concentration for the impurity with larger lattice and decrease with the impurity concentration for the impurity with smaller lattice; and

(iii) For KDP added with inorganic impurities having no common ion and organic impurities, the nucleation parameters increase with the impurity concentration regardless of density or lattice size of the impurity.

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